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THE PREPARATION OF (NP(P-OC6H4LI)2)3 BY METAL -HALOGEN EXCHANGE--ETC(U)  
NOV 78 T L EVANS, T J FULLER, H R ALLCOCK N00014-75-C-0685

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EXCHANGE, AND ITS REACTIONS WITH ELECTROPHILES

by

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Accepted for publication in the  
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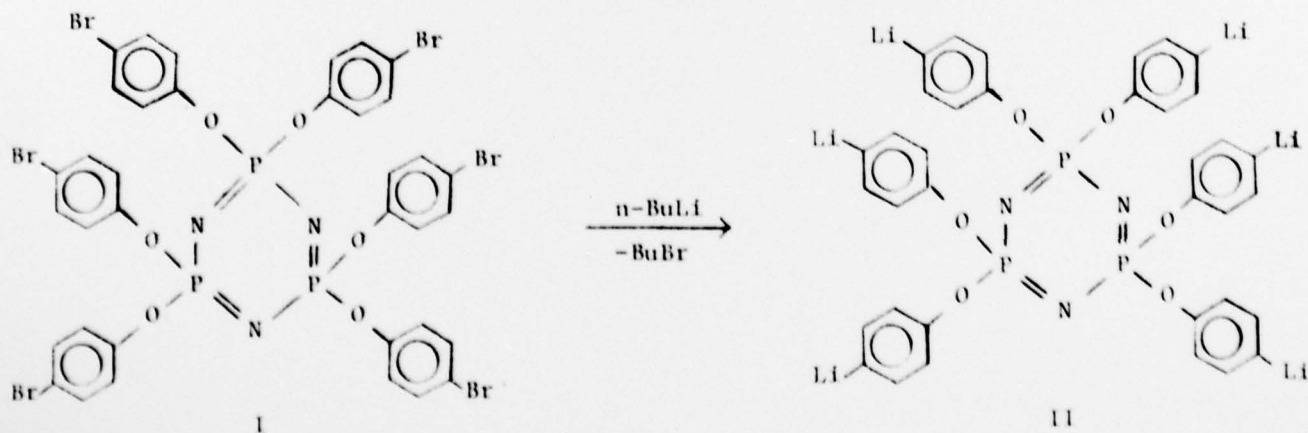
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The Preparation of  $[\text{NP}(\text{p-OC}_6\text{H}_4\text{Li})_2]_3$  by Metal-Halogen  
Exchange, and Its Reactions with Electrophiles

Sir:

The reactions of cyclic and polymeric halophosphazenes with organolithium reagents have been studied extensively,<sup>1,2,3</sup> but the reactions of organo-metallic reagents with cyclic and polymeric organo-functional phosphazenes have not been explored in detail. Of particular interest to us were reactions that could yield carbanionic species bound directly to phosphazene cyclic and polymeric compounds. Such reactive intermediates could be used to synthesize a wide range of new cyclic and high polymeric phosphazenes not accessible by other synthetic routes, including those that might form unusual ligands for transition metals.

We have found that hexa(p-bromophenoxy)cyclotriphosphazene, (I), undergoes a high yield metal-halogen exchange reaction with *n*-butyllithium to yield the hexalithio derivative, (II). The reaction conditions employed involved a rapid addition of *n*-butyllithium (1.6 M in hexane) in a 15% excess to a tetrahydrofuran solution of (I) at  $-40^\circ\text{C}$ .





The presence of (II) was confirmed by its reactions at  $-40^{\circ}\text{C}$  with electrophiles, such as deuterium oxide, carbon dioxide, chlorodiphenylphosphine and triphenyltin chloride to yield the following derivatives:  $[\text{NP}(\text{p-OC}_6\text{H}_4\text{D})_2]_3$ , (III);  $[\text{NP}(\text{p-OC}_6\text{H}_4\text{COOH})_2]_3$ , (IV);  $[\text{NP}(\text{p-OC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2)_2]_3$ , (V); and  $[\text{NP}(\text{p-OC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_5)_3)_2]_3$ , (VI). All of these compounds were identified by  $^{31}\text{P}$  nmr spectra, infrared spectra, and chemical analysis. The position of lithium incorporation on the aromatic ring was confirmed by the  $^{13}\text{C}$  nmr spectrum of compound (III) which revealed both the presence of a triplet structure and a decrease in the resonance signal for the carbon at the para position of the aromatic unit when compared with the  $^{13}\text{C}$  nmr spectrum of  $[\text{NP}(\text{OC}_6\text{H}_5)_2]_3$ .<sup>4</sup> The absence of significant skeletal cleavage during metallation is a considerable advantage for the use of such processes in phosphazene high polymer syntheses.

The binding of metal complexes to phosphazene compounds is of structural, catalytic, and potential biomedical importance.<sup>5,6</sup> This reaction system possesses a capacity for the binding of metals both through reactions of (II) with metal halides, as demonstrated by the synthesis of compound (VI), and through the reactions of compound (V) with metal complexes. In order to illustrate this second reaction pathway, (V) was allowed to react with  $\text{H}_2\text{Os}_3(\text{CO})_{10}$ , (VII), a compound which has been demonstrated previously to react with tertiary phosphines to yield mono-substituted phosphine osmium cluster compounds,  $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{PR}_3)$ .<sup>7</sup> The high reactivity of this osmium cluster (VII) was ascribed to a metal-metal double bond.<sup>8</sup> When compound (V) was allowed to react with a deficiency of (VII) at  $25^{\circ}\text{C}$  in methylene chloride solvent, the expected color change from violet to yellow was observed. Furthermore, infrared spectral comparisons of the carbonyl stretching regions for the osmium complex derived

from triphenylphosphine and that derived from (V) confirmed the existence of metal binding through the phosphine residues of (V) rather than through the skeletal nitrogen atoms.

Experiments are now underway in our laboratory to extend these small molecule cyclic model reactions to high polymeric phosphazenes.

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#### References and Notes

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